Mathematical Modelling, Vol. 2, pp. 283–294, 1981
Printed in the USA.

0270-0255/81/040283-12$02.00/0

MODELLING MAGNETIC CIRCULAR DICHROISM WITH APPLICATION TO IMIDAZOLES

YUNG-CHANG YIM,* D. J. CALDWELL,† and HENRY EYRING

Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Communicated by Henry Eyring

(*Received March 1981*)

Abstract—The magnetic circular dichroism of imidazole and its derivatives are calculated using the π-electron approximation, where the resonance integral is computed by using the formula

$$h_{\mu\nu} = \frac{\hbar^2}{m}(1 - S_{\mu\nu}^2)\,\mathbf{R}_{\mu\nu} \cdot \nabla_{\mu\nu}/R_{\mu\nu}^2 + \tfrac{1}{2}S_{\mu\nu}(h_{\mu\mu} + h_{\nu\nu})$$

plus higher order terms. The magnetic circular dichroism (MCD) spectra for the molecules are also presented. As a complementary procedure to the π-electron calculation, Michl's perimeter model [1] for predicting the signs of the MCD is employed.

INTRODUCTION

The imidazole ring is a model chromophore for biological compounds which contain heteroatoms such as nitrogen. The imidazoles were studied by comparing measured with calculated ultraviolet (UV) and MCD spectra along with energies and spectral intensities.

The *A* term [2, 3, 4] of MCD arises when the excited state is degenerate, and the *C* term arises when the ground state is degenerate. The *B* term of MCD describes the effect of mixing two or more states.

Since molecules which have closed-shell ground states are nondegenerate, the *C* term will not be considered here. The *A* and *B* terms of MCD are given by

$$B(o \to n) = \mathrm{Im}\left\{\sum_{s \neq n} \frac{\boldsymbol{\mu}_{on} \cdot \mathbf{M}_{ns} \times \boldsymbol{\mu}_{so}}{E_s - E_n} + \sum_{s \neq o} \frac{\boldsymbol{\mu}_{on} \times \boldsymbol{\mu}_{so} \cdot \mathbf{M}_{ns}}{E_s - E_o}\right\} \tag{1}$$

$$A(o \to n) = \sum_{n'} \{(\mathbf{M}_{n'n'} - \mathbf{M}_{oo}) \cdot \mathrm{Im}\,\boldsymbol{\mu}_{on'} \times \boldsymbol{\mu}_{n'o}\} \tag{2}$$

where

$$\boldsymbol{\mu}_{on} = \left\langle \Phi_o \middle| \sum_i e\mathbf{r}_i \middle| \Phi_n \right\rangle$$

*This work is based on the dissertation submitted to the University of Utah in partial fulfillment of the requirements for the degree of Ph.D.

†Present address: Hercules Incorporated, Magna, Utah 84044.

and the magnetic dipole transition moment is given by

$$\mathbf{M}_{ns} = \left\langle \Phi_n \left| \sum_i \frac{c}{2m_i c} \mathbf{r}_i \times \mathbf{P}_i \right| \Phi_s \right\rangle.$$

Here $\mathbf{r}_i$ is the position vector of electron i, and $\mathbf{p}_i$ is the linear momentum operator for electron i. When Φ_n is doubly degenerate, the pair of states can be taken as complex conjugates:

$$\Psi_+ = \frac{1}{\sqrt{2}}(\Psi_{n_1} + i\Psi_{n_2})$$

and

$$\Psi_- = \frac{1}{\sqrt{2}}(\Psi_{n_1} - i\Psi_{n_2}).$$

Then Eq. (2) becomes

$$A(o \to n) = 2\mathrm{Im}\{(\boldsymbol{\mu}_{on_1} \times \boldsymbol{\mu}_{n_2 o}) \cdot \mathbf{M}_{n_1 n_2}\}. \tag{3}$$

This allows Eq. (1) to be rewritten as

$$B(o \to n_1) = \mathrm{Im}\left\{\frac{\boldsymbol{\mu}_{on_1} \cdot \mathbf{M}_{n_1 n_2} \times \boldsymbol{\mu}_{n_2 o}}{E_s - E_{n_1}} + \frac{\boldsymbol{\mu}_{on_1} \times \boldsymbol{\mu}_{n_2 o} \cdot \mathbf{M}_{n_1 n_2}}{E_{n_2} - E_o}\right\}$$
$$+ \mathrm{Im}\left\{\sum_{s(\neq n_1, n_2)} \frac{\boldsymbol{\mu}_{on_1} \cdot \mathbf{M}_{n_1 s} \times \boldsymbol{\mu}_{so}}{E_s - E_{n_1}} + \sum_{s(\neq n_2, o)} \frac{\boldsymbol{\mu}_{on_1} \times \boldsymbol{\mu}_{n_2 o} \cdot \mathbf{M}_{n_1 n_2}}{E_{n_2} - E_o}\right\} \tag{4}$$

When E_{n_2} and E_{n_1} are nearly degenerate, the difference $\Delta E_{21} = E_{n_2} - E_{n_1}$ is very small and $\Delta E_{s1} = E_s - E_{n_1}$ is large; thus the contribution from the second term on the right-hand side of Eq. (4) to $B(o \to n_1)$ is relatively small, and the first term determines the magnitude and sign of the B term.

When the above condition is satisfied one may write

$$B(o \to n_1) f(\omega, \omega_{on_1}) + B(o \to n_2) f(\omega, \omega_{on_2}) \simeq A(o \to n) f^1(\omega, \omega_{on}). \tag{5}$$

The mathematical expressions of the A term and B term under these circumstances are equvalent even though the origins of the A term and B term are different. Here the line shape functions f and f^1 [5, 6] are given by

$$f(\omega, \omega_{oj}) \cong \frac{\omega^3 \Gamma_{oj}}{(\omega_{oj}^2 - \omega^2)^2 + \omega^2 \Gamma_{oj}^2} \tag{6}$$

$$f^1(\omega, \omega_{oj}) = \frac{\partial f}{\partial E} = \frac{4\omega_{oj}^4(\omega_{oj}^2 - \omega^2)}{h[(\omega_{oj}^2 - \omega^2)^2 + \omega^2 \Gamma_{oj}^2]^2}, \tag{7}$$

where $E = h\omega$, and Γ is a natural line width.

THE COMPUTATIONAL METHOD

For the computation of the transition dipole moments, the following formulas [7] are used:

$$\langle a|\mathbf{r}|j\rangle = \frac{\hbar^2}{m}\langle a|\nabla|j\rangle/(E_j - E_a) \tag{8}$$

$$\langle a|\nabla|j\rangle = \frac{m}{\hbar^2}\langle a|[\mathbf{r}, F]|j\rangle, \tag{9}$$

where $[\mathbf{r}, F]$ is the quantum Poisson bracket, F is the Fock operator, and E_j is the eigenvalue of the molecular orbital Ψ_j for the Fock operator $F\Psi_j = E_j\Psi_j$.

The transition magnetic moment [10] is given by

$$\langle a|\mathbf{m}|j\rangle = \sum_i \frac{e}{2m_i c}\langle a|\mathbf{r}_i \times P_i|j\rangle$$

$$= \sum_i \sum_{\alpha>\beta} \frac{e}{2m_i c}(C_{\alpha a}C_{\beta j} - C_{\beta a}C_{\alpha j})\langle \alpha|\mathbf{r}_i \times P_i|\beta\rangle, \tag{10}$$

where $C_{\alpha a}$ is the expansion coefficient of the molecular orbital,

$$\Psi_a = \sum_\alpha C_{\alpha a}\phi_\alpha.$$

The subscripts in italic letters indicate molecular orbitals and Greek letters indicate the atomic orbitals.

The matrix elements of the angular momentum can be computed using the following formula [11]:

$$\langle \alpha|\mathbf{r} \times \nabla|\beta\rangle = \frac{m}{\hbar^2}\langle \alpha|\mathbf{r} \times [\mathbf{r}, h]|\beta\rangle = -\frac{m}{\hbar^2}\langle \alpha|\mathbf{r} \times h\mathbf{r}|\beta\rangle$$

$$\simeq -\frac{m}{\hbar^2}\sum_{\sigma,\rho} \mathbf{R}_\alpha \times \mathbf{R}_\beta h_{\rho\sigma}\delta_{\alpha\rho}\delta_{\rho\beta}$$

$$= -\frac{m}{\hbar^2}\mathbf{R}_\alpha \times \mathbf{R}_\beta h_{\alpha\beta}. \tag{11}$$

However, Eq. (11) depends on the choice of an origin. A procedure to avoid the origin dependence can be obtained from the following considerations:

$$\langle a|\mathbf{r} \times \nabla|j\rangle = \sum_k \langle a|\mathbf{r}|k\rangle \times \langle k|\nabla|j\rangle$$

$$= \sum_{k\neq a} \langle a|\mathbf{r}|k\rangle \times \langle k|\nabla|j\rangle + \langle a|\mathbf{r}|a\rangle \times \langle a|\nabla|j\rangle. \tag{12}$$

The origin dependence is due to the second term of Eq. (12). The dipole moment [12] of state Ψ_a is given by

$$\mu_{aa} = \left\langle a\left|\sum_i Z_i\mathbf{R}_i - \sum_i \mathbf{r}_i\right|a\right\rangle, \tag{13}$$

where Z_i is the effective nuclear charge at atom i, and $\mathbf{R}_i$ is the position vector of atom i.

Since the dipole moment is the vector distance between the positive and negative charge centers, an origin independent term may be obtained by subtracting

$$\left\langle a \left| \sum_i Z_i R_i \right| a \right\rangle$$

from $\langle a|\mathbf{r}|a\rangle$ in Eq. (12), giving

$$\langle a|\mathbf{r}\times\nabla|j\rangle = \sum_{k\neq a} \langle a|\mathbf{r}|k\rangle \times \langle k|\nabla|j\rangle + \langle a| - \sum_i Z_i \mathbf{R}_i + \mathbf{r}|a\rangle \times \langle a|\nabla|j\rangle. \tag{14}$$

This equation indicates that the magnetic moment of a molecule arises from the circulation of the electron cloud around the center of positive charge in the same way as the atomic magnetic moment. For the calculation of the resonance integral in the Fock matrix we use the following formula

$$h_{\mu\nu} = \epsilon_{\mu\nu} + \tfrac{1}{2}(h_{\mu\mu} + h_{\nu\nu}) S_{\mu\nu}, \tag{15}$$

where

$$\epsilon_{\mu\nu} = (1 - S_{\mu\nu}^2)\beta_{\mu\nu} + \tfrac{1}{2}\sum \{[(\mathbf{R}_{\mu\nu}\cdot\mathbf{R}_{i\nu})S_{i\nu}\beta_{\mu i} + (\mathbf{R}_{\mu\nu}\cdot\mathbf{R}_{i\mu})S_{i\mu}\beta_{\nu i}]/R_{\mu\nu}^2 + \tfrac{1}{2}S_{\mu i}h_{ii}S_{i\nu}\}.$$

The above relation is obtained by the Heisenberg equation of motion,

$$\dot{\mathbf{P}} = \left(\frac{im}{\hbar}\right)[h, \mathbf{r}],$$

and a modified formula of the Dirac resolution of the identity as

$$\sum_{\mu,\nu} |\chi_\mu\rangle S_{\mu\nu}^{-1} \langle\chi_\mu| = 1$$

for the nonorthogonal basis set. Also

$$\beta_{\mu\nu} = \frac{\hbar^2}{m}\mathbf{R}_{\mu\nu}\cdot\mathbf{V}_{\mu\nu}\Big/ R_{\mu\nu}^2, \nabla_{\mu\nu} = \frac{\partial S_{\mu\nu}}{\partial R_{\mu\nu}}.$$

The matrix element $h_{\mu\nu}$ for the nonorthogonal basis set is transformed into $h_{\mu\nu}^\lambda$ for the orthogonal set (1) as follows:

$$h_{\mu\nu}^\lambda = \sum_{\rho,\sigma} S_{\mu\rho}^{-1/2} \epsilon_{\rho\sigma} S_{\sigma\nu}^{-1/2} + \tfrac{1}{2}(S^{1/2}H^\circ S^{-1/2} + S^{-1/2}H^\circ S^{1/2}) \tag{16}$$

where H° is a diagonal matrix with elements H_{ii}. The repulsion integrals are computed for the orthogonal basis set using the modified Mataga–Nishimoto formula [17]:

$$\gamma_{\mu\nu}^\lambda = \sum_{\rho\sigma} S_{\mu\rho}^{-1/2} S_{\mu\rho}^{1/2} \gamma_{\rho\sigma} S_{\sigma\nu}^{1/2} S_{\sigma\nu}^{-1/2} \tag{17}$$

$$\gamma_{\rho\sigma} = 14.397\left(\frac{28.794}{\gamma_{\rho\rho} + \gamma_{\sigma\sigma}} + \tau R_{\mu\nu}\right)^{-1}. \tag{18}$$

Michl [1, 15, 16, 17] has shown that a simple perimeter model in a perturbed molecular orbital (PMO) theory can be used to rationalize and predict trends in the MCD spectra of a system having $(4N+2)$-electrons such as $[n]$ annulene and heterocyclic analogs with a single electron donating or withdrawing substituent. In order to make the problem simple, one may consider only the transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). For a system with $0 < N < (n/2-1)$, there are two degenerate HOMOs and two LUMOs in the unperturbed perimeter. For a degenerate system it is convenient to express a molecular orbital (MO) by a complex form such as

$$\Psi_k = (\phi_k + i\phi_k^{\perp})/\sqrt{2}$$

$$\Psi_{-k} = (\phi_k - i\phi_k^{\perp})/\sqrt{2},$$

where $k = 0, 1, 2$, etc., and ϕ_k and $\phi_k^{\perp}$ are a pair of degenerate real MOs, while Ψ_k and Ψ_{-k} are the degenerate complex MOs. For the perimeter there are four relevant excitations, $\psi_N \rightarrow \psi_{N+1}$, $\psi_{-N} \rightarrow \psi_{-N-1}$, $\psi_N \rightarrow \psi_{-N-1}$, $\psi_{-N} \rightarrow \psi_{N+1}$. In ψ_{-k} ($k \neq 0$, $k \neq n/2$, for even n, $k \neq 0$, for odd n) two electrons circulate clockwise, while in ψ_k two electrons circulate counterclockwise. In the transition $\psi_N \rightarrow \psi_{N+1}$, left-handed circular polarized light is absorbed while for $\psi_{-N} \rightarrow \psi_{-N-1}$, right-handed circular polarized light is absorbed in the excitations. These transitions are degenerate; therefore they occur at the same energy. Before the excitation, the magnetic moment due to the circulation of the electron in ψ_N is exactly cancelled by the moment due to the electron in ψ_{-N}, but the moment in ψ_{N+1} may be increased or decreased, so that the cancellation is no longer exact. For the most common combinations of n and N values, the loop current is slightly higher in the LUMOs than in the HOMOs; thus the magnetic moment in $\psi_N \rightarrow \psi_{N+1}$ is weakly positive. In the presence of a static magnetic field H, perpendicular to the plane of the perimeter and upward toward the viewer there is the Zeeman splitting given by

$$\Delta E(\psi_N \rightarrow \psi_{N+1}) = \boldsymbol{\mu}^- \cdot \mathbf{H}$$

and

$$\Delta E(\psi_{-N} \rightarrow \psi_{-N-1}) = -\boldsymbol{\mu}^- \cdot \mathbf{H},$$

while in $\psi_{-N} \rightarrow \psi_{N+1}$, the magnetic moment is large and negative and the moment of $\psi_N \rightarrow \psi_{-N-1}$ is large and positive. Thus the Zeeman splitting in the sense reversing excitation will be

$$\Delta E(\psi_{-N} \rightarrow \psi_{N+1}) = \boldsymbol{\mu}^+ \cdot \mathbf{H}'$$

and

$$\Delta E(\psi_N \rightarrow \psi_{-N-1}) = -\boldsymbol{\mu}^+ \cdot \mathbf{H},$$

where $\boldsymbol{\mu}^-$ and $\boldsymbol{\mu}^+$ denote the magnetic moments due to the sense preserving excitation and the sense reversing excitation, respectively. Ordinarily the contribution to B terms from $\boldsymbol{\mu}^+$ is larger than from $\boldsymbol{\mu}^-$. Moreover, the contribution from the $\boldsymbol{\mu}^-$ is structure

independent. The contribution from μ^+ depends on the degree to which the splitting of the HOMOs (ΔHOMO) of the original [n] annulene perimeter differs from the splitting of its LUMOs (ΔLUMO). ΔHOMO reflects the hindrance to the circulation of the positive hole which the promoted electron leaves behind in HOMO, and ΔLUMO reflects the hindrance to the circulation of the excited electron in LUMO. Obviously, ΔHOMO and ΔLUMO are induced by the perturbation which converts the perimeter into the actual molecule. If ΔHOMO = ΔLUMO, the contribution to the B term, which is proportional to μ^+, vanishes; if ΔHOMO < ΔLUMO, electron circulation dominates, and the μ^+ contributions to B terms of the four transitions are +, −, +, − in the order of increasing energy L_1, L_2, B_1, B_2. If ΔHOMO < ΔLUMO, hole circulation dominates, and the μ^+ contributions to the B terms of the four transitions are −, +, −, + for L_1, L_2, B_1, B_2. Here L_1, L_2, B_1, and B_2 have been used to label the L band and B band (19) in the order of increasing energy. The relative size of ΔHOMO and ΔLUMO can be derived from the orbital interaction in the first order PMO theory. The chromophores are classified into three categories by the difference between ΔHOMO and ΔLUMO. If ΔHOMO ≅ ΔLUMO, the chromophore is soft; if ΔHOMO < ΔLUMO, the chromophore is positive hard; if ΔHOMO < ΔLUMO, the chromophore is negative hard. The signs of A or B terms of the soft chromophore are most easily effected by the perturbation. The electron withdrawing substituents react primarily with ΔLUMO ($+E$ mesomeric effect) as the electron donating substituents do with ΔHOMO ($-E$ mesomeric effect).

The positions of a soft chromophore are classified with respect to substituent effects on ΔLUMO as $+E$-dominant (D) if $C^2_{-1} > C^2_{-2}$, $+E$-subdominant (S) if $C^2_{-1} < C^2_{-2}$, and $+E$-neutral (N) if $C^2_{-1} \cong C^2_{-1}$. Similarly, they are classified with respect to effects on ΔHOMO as $-E$-dominant if $C^2_1 > C^2_2$, $-E$-subdominant if $C^2_1 < C^2_2$, and $-E$-neutral if $C^2_1 \cong C^2_2$. Here the four front orbitals are labelled 2, 1, −1, −2 in increasing order of energies. The inductive effects are determined by

$$(\Delta\text{HOMO}-\Delta\text{LUMO})/(-\Delta\alpha) = C^2_2 - C^2_1 + C^2_{-2} - C^2_{-1}.$$

The procedure described above, which counts the signs of the observed spectra, is an interesting complementary method to our direct calculations of the imidazole series.

RESULTS AND DISCUSSION

The MCD spectra reported here were measured with a modified Cary Model 60 recording spectropolarimeter equipped with a Varian superconducting solenoid system, which produces a magnetic field of 45 kG. The concentration of the solutions measured ranged from 0.1 to 0.5 mg/ml in order that polymerization could be avoided. The atomic coordinates were taken from crystallographic data, and calculations were performed with a 96 kbit mapped system of the PDP 11/45.

The A terms and B terms of MCD and the energy value of the experimental and calculated results are shown in Table 1. All the spectra measured in this work are shown in Figs. 1 to 12.

The calculated results show that the dipole moments of two low-lying transitions (203 and 183 nm) are perpendicular to each other. This is expected from the C_{2v} character table where the allowed two transitions A_1 and B_1 are mutually perpendicular.

The substituent effect of the imidazole on the overall spectrum depends on how strongly they tend to resonate with the chromophore. The experimental and calculated results show that they agree quite well as to magnitudes and signs. The MCD signs of all the molecules we measured can be best described by the ΔHOMO–ΔLUMO concept [1, 15], as mentioned before. For the strongly electron circulation dominated transitions

Table 1. Calculated and experimental results for imidazoles.

	Energy (nm)		Oscillator Strength		A Term ($D^2\beta$)		B Term $\left(\frac{D^2\beta}{cm^{-1}} \times 10^4\right)$	
Imidazole	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
2-H	203	207	0.133	0.133	17.9	17.9	—	—
		183		0.193				
2-CH_3	208	—	0.316	—	23.0	—	—	—
4-CH_3	213	—	0.075	—	18.2	—	—	—
2-NO_2	320	296	0.177	0.136	—	—	−7.04	−6.13
	275	253	—	0.049	—	—	0.29	0.79
	220	222	0.076	0.143	—	—	2.78	4.70
4-NO_2	300	285	0.167	0.143	—	—	−2.48	−3.56
	266	257	0.045	0.027	—	—	0.33	1.3
	223	213	0.067	0.017	—	—	0.58	0.17
2,4-OH	—	247	—	0.213	—	23.4	—	—
2,4,5-OH	—	276	—	0.271	—	28.6	—	—
2-NH_2	—	230	—	0.208	—	26.4	—	—
4-NH_2	—	268	—	0.267	—	29.6	—	—
5-NH_2	—	235	—	0.226	—	28.4	—	—
2,4-NH_2	—	255	—	0.254	—	26.0	—	—
2,4,5-NH_2	—	283	—	0.311	—	30.3	—	—
4-Cl	220	—	0.080	—	19.6	—	—	—
4,5-Cl	223	—	0.112	—	23.9	—	—	—
4-Br	217	—	0.80	—	20.6	—	—	—
2-SH	253	—	0.320	—	13.5	—	—	—

(hard positive chromophore; ΔHOMO > LUMO), the *A* terms or the *B* terms are not easily disturbed by a weak perturbing substituent. The π-electron calculation shows that the imidazole chromophore is positive hard (ΔHOMO − ΔLUMO = 0.71 eV), so that the signs of the *B* term of the imidazole will not be easily changed by the weak substituent effect. The positions of the imidazole are labelled as in Fig. 13. The positions of the imidazole substituents are shown in Table 2. The values in Table 2 are obtained from the MOs of the π-electron calculation.

Position 2 is the *dD* type (the first lower case *d* is for a weak $+E$ dominant, and the next *D* is for the $-E$ dominant) so that electron donating substituents such as $-CH_3$, −Cl, −Br, and −SH will produce more positive *B* terms for the lowest transitions. The −SH is an especially strong electron donating substituent; thus the *B* term of the mercapto derivative will be correspondingly large. Position 4 is the *Sd* (*S* for the $+E$ subdominant, and *d* for $-E$ weak dominant) so that the effects of the substituents at position 4 are less positive than those of position 2 of the imidazole. However, the derivatives will have larger *B* terms than the parent imidazole at both positions for the lowest transition (+, − in an increasing order of energies). Position 4 is of the *Sd* type. Therefore, the interaction between a strong electron withdrawing substituent and LUMO will change the positions of LUMOs and increase ΔLUMO. Thus substituents such as $-NO_2$ will reverse the sign of the *B* term of imidazole even though it is a positive hard chromophore. As a result of substitution the *B* term of 4-nitroimidazole will have a negative value for the lowest transition. These predictions for the imidazole derivatives agree nicely with the experimental results. The benzimidazole can be obtained from the idenide anion by replacement of $-CH^--$ at position 1 and −CH= at position 3 by −NH− and −N=, respectively The numbering of the positions of the indenide anion is shown in Fig. 14. Positions 1 and 3 are of *ND type* (2). The inductive effect by double substitution of heteroatom N will produce a negative value of the *B* term of the benzimidazole, because the indenide anion is a soft chromophore (ΔHOMO ≅ ΔLUMO).

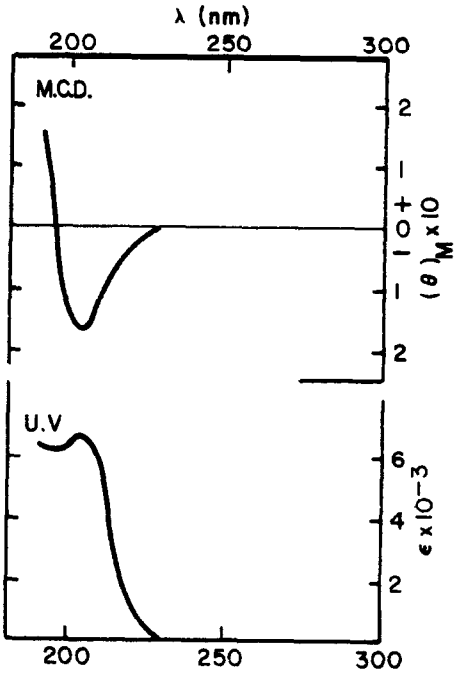

Fig. 1. Imidazole in H_2O.

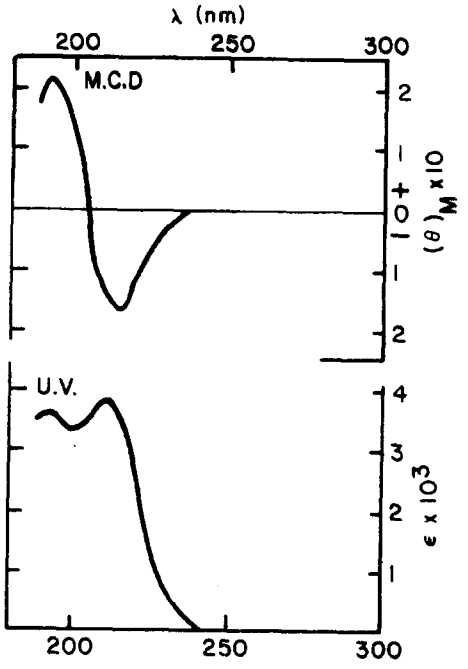

Fig. 2. Chloroimidazole in H_2O.

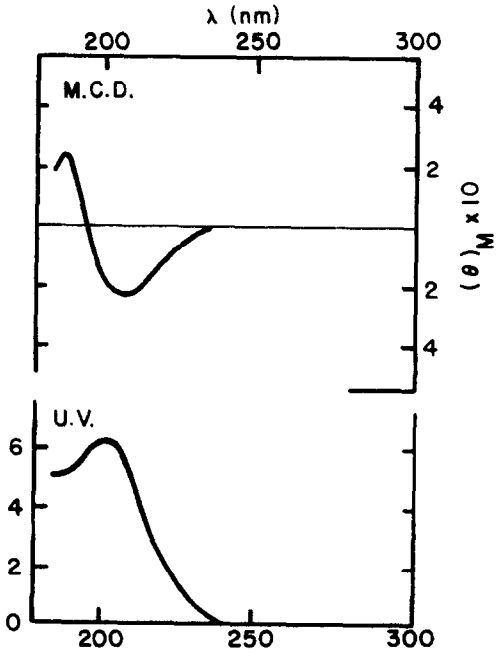

Fig. 3. Methylimidazole in H_2O.

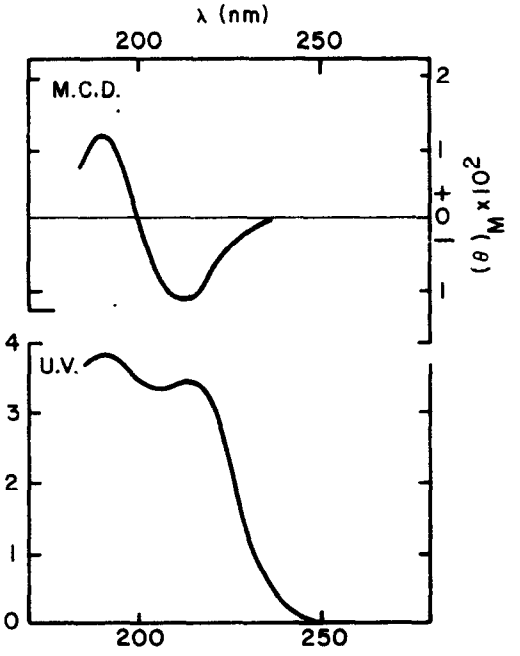

Fig. 4. 4-Methylimidazole in H_2O.

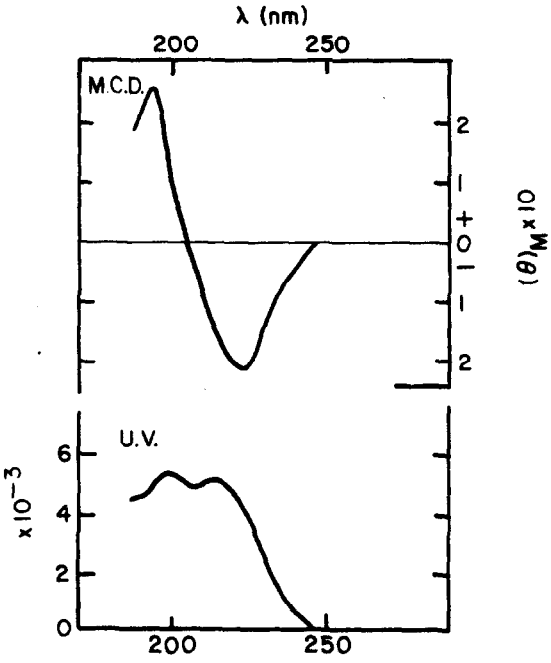

Fig. 5. 4.5-Dichlorimidazole in H_2O.

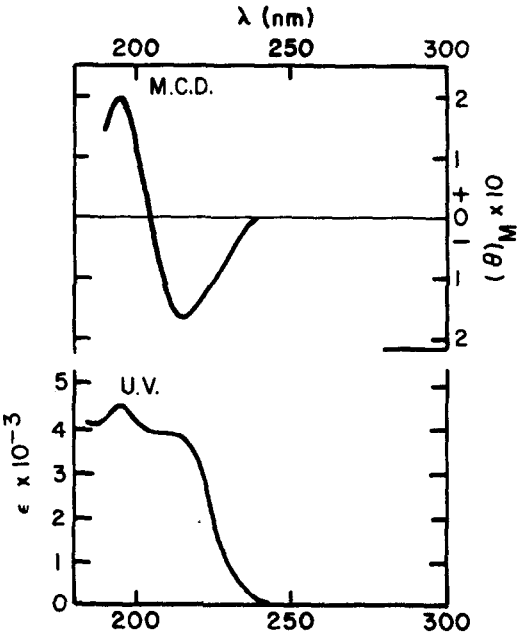

Fig. 6. 4-Bromoimidazole in H_2O.

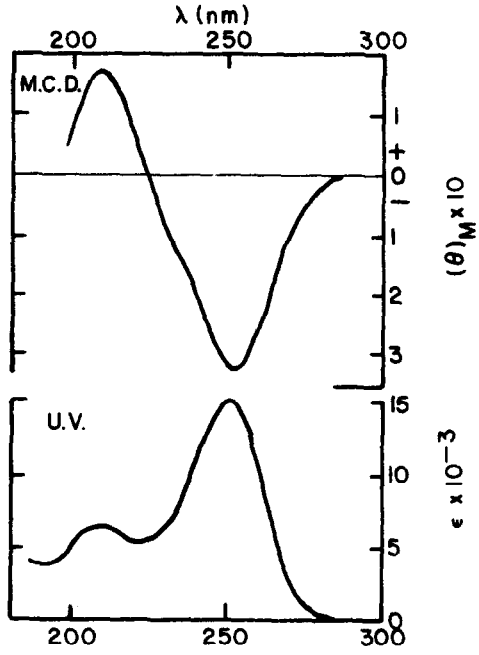

Fig. 7. 2-Mercaptoimidazole in H_2O.

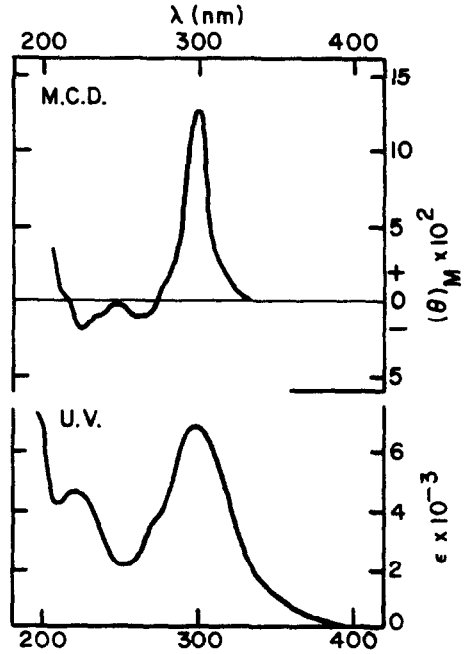

Fig. 8. 4-Nitroimidazole in H_2O.

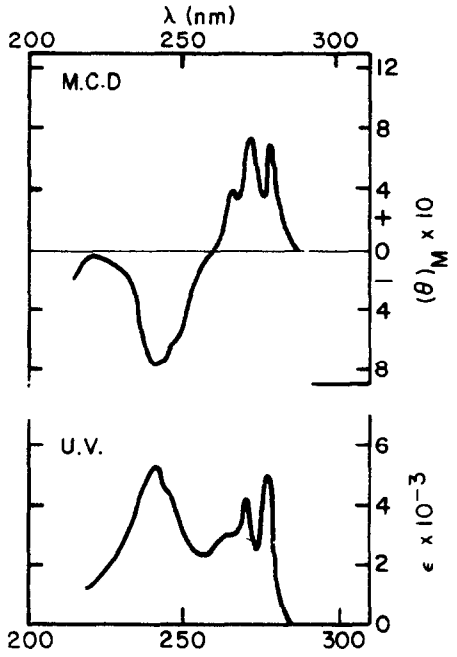

Fig. 9. Benzimidazole in methanol.

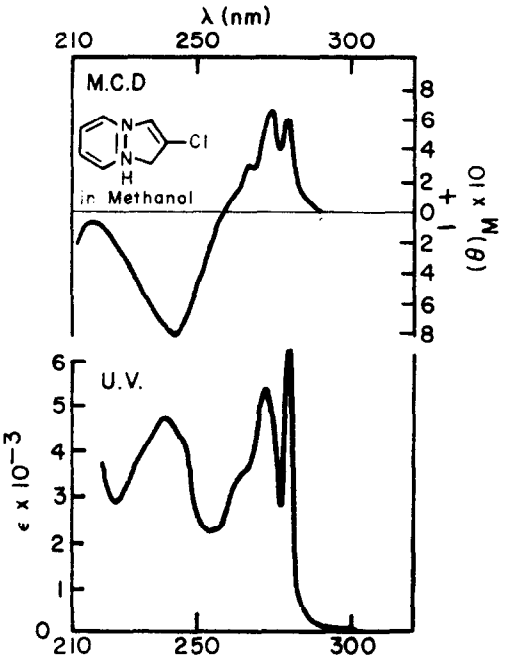

Fig. 10. 2-Chlorobenzimidazole in methanol.

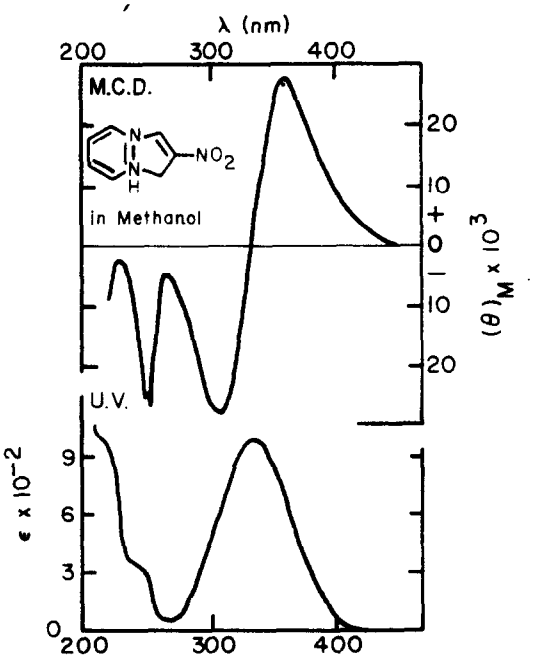

Fig. 11. 2-Nitrogenzimidazole in methanol.

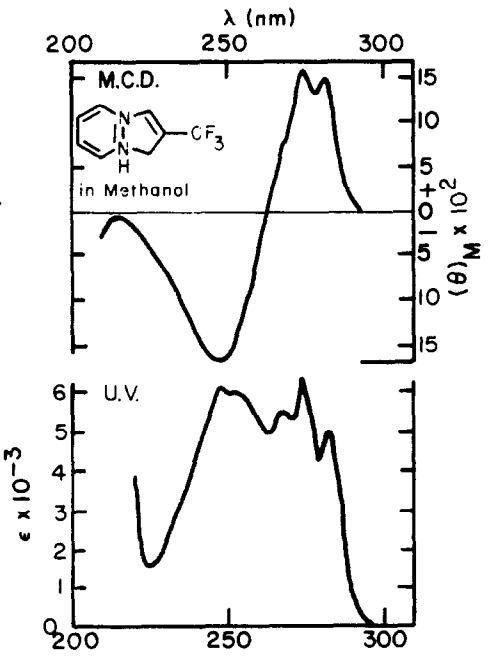

Fig. 12. 2-Triflorobenzimidazole in methanol.

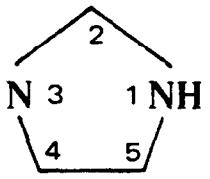

Fig. 13. Positions of the imidazole.

Table 2. Characteristic positions in the imidazole with respect to the mesomeric substituent effect.

Position	1	2	3	4	5
$C^2_{-1} - C^2_{-2}(+E)$	0.176	0.178	−0.221	−0.279	0.145
$C^2_1 - C^2_2(-E)$	−0.397	0.240	−0.353	0.147	0.364
Position Type	*dS*	*dD*	*sS*	*Sd*	*dD*

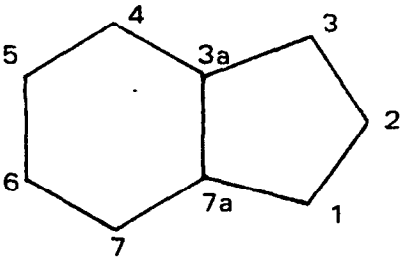

Fig. 14. Positions of the indenide anion.

SUMMARY

The formula used to calculate the resonance integrals produces slightly higher values than commonly used β_π values in the semiempirical calculations, but the agreement with ones obtained from the experimental results is very good. The resonance integrals for the benzene molecule are exactly the same as the experimental values.

A center of positive charge is chosen as an origin for the calculation of molecular angular momentum in MCD. This gives the interpretation of the physical origin of molecular angular momentum for planar molecules.

The Michl perimeter model for the preduction of the signs of MCD of the substituent effect is an important complementary method to the conventional π-electron approximation. This method gives quite good agreement with the experimental MCD in signs.

Acknowledgement—We acknowledge the support of this work by the National Science Foundation (Grant No. 7617836) and the National Institutes of Health (CM 12862-16). We are indebted also to Professor J. Michl for calling our attention to his interesting method of estimating π-electron MCD.

REFERENCES

1. J. Michl, Electronic structure of aromatic π-electron systems as reflected in their MCD spectra. *Pure Appl. Chem.* **52**, 1549 (1980).
2. P. J. Stephens, Excited state magnetic moments through moment analysis of magnetic circular dichroism. *Chem. Phys. Lett.* **2**, 241 (1968).

3. R. Serber, Theory of the Faraday effect in molecules. *Phys. Rev.* **41**, 489 (1932).
4. A. D. Buckinghap and P. J. Stephens, Magnetic optical activity. *Annu. Rev. Phys. Chem.* **17**, 399 (1966).
5. P. J. Stephens, Theory of magnetic circular dichroism. *J. Chem. Phys.* **52**, 3489 (1970).
6. W. Heitler, *The Quantum Theory of Radiation*, 3rd Ed., p. 182, Oxford University, London (1954).
7. H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry*, p. 111, Wiley, New York (1944).
8. L. I. Schiff, *Quantum Mechanics*, 2nd Ed., Sec. 50, McGraw-Hill, New York (1955).
9. C. C. J. Roothaan, New developments in molecular orbital theory. *Rev. Mod. Phys.* **23**, 69 (1951).
10. H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry*, p. 114, Wiley, New York (1944).
11. J. Linderberg and L. Seamans, Magneto-optical activity; gauge-invariant calculations in the random phase approximation. *Mol. Phys.* **24**, 1393 (1973).
12. F. L. Pilar, *Elementary Quantum Chemistry*, p. 637, McGraw-Hill, New York (1968).
13. J. Linderberg, Consistancy requirement in the Pariser-Parr-Pople model. *Chem. Phys. Lett.* **1**, 39 (1967).
14. K. Nishimoto and M. Mataga, Electronic structure and spectra of nitrogen heterocycles, *Z. Phys. Chem.* (*Frankfurt*) **12**, 335; **13**, 140 (1957).
15. S. L. Wallace and J. Michl, Magnetic circular dichroism of cyclic π-electron systems—20 amino derivatives of indole–azindole and purine. *Tetrahedron* **36**, 1531 (1980).
16. J. Michl, Magnetic circular dichroism of cyclic π-electron systems. 1. Algebraic solutions of the perimeter model for the *A* and *B* terms of high symmetry systems with a $(4N + 2)$ electron (n) annulene perimeter. *J. Am. Chem. Soc.* **100**, 6801 (1978).
17. J. Michl, Magnetic Circular dichroism of cyclic π-electron systems. 2. Algebraic solution of the perimeter model for the *B* terms of systems with a $(4N + 2)$-electron (n) annulene perimeter. *J. Am. Chem. Soc.* **100**, 6812 (1978).
18. J. R. Platt, Classification of spectra of cata-condensed hydrocarbons. *J. Chem. Phys.* **17**, 484 (1949).